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"Spectroscopic and Structural Properties of Binuclear Platinum-Terpyridine Complexes"

by

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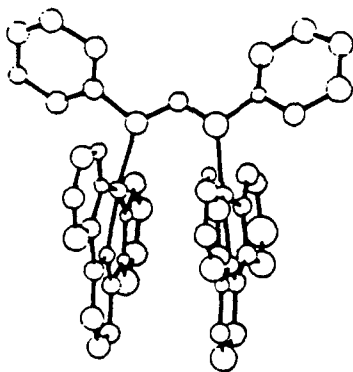
SPECTROSCOPIC AND STRUCTURAL PROPERTIES OF  
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*Contribution No. 8696 from the Arthur Amos Noyes Laboratory,  
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Synopsis

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**Abstract.**

Binuclear complexes of the platinum(terpyridine) fragment have been prepared with a variety of bridging ligands to form the cationic species  $\{[\text{Pt}(\text{tpy})]_2(\mu\text{-L})\}^{3+}$  (tpy = 2,2'-6,2'-terpyridine; LH = pyrazole **1**, azaindole **2**, diphenylformamidine **3**). These complexes, along with the previously reported arginine-bridged species **4** (Kostic *et al.*, *Inorg. Chem.* 1990, 29, 918), have been characterized spectroscopically. The lowest energy electronic absorption is assigned to a  $d\sigma^* \rightarrow \pi^*(\text{tpy})$  (metal-to-ligand charge transfer, MLCT) transition; the transition energy decreases with decreasing Pt-Pt distance, according to **1** (430; 3.432) > **2** (460; 3.13) > **3** (490; 3.049) > **4** (488 nm; 2.998Å). Emission is observed from the  $^3(d\sigma^*\pi^*)$  state of complexes **2**, **3**, and **4**. Low-temperature glassy solutions of complex **1** also exhibit  $^3(d\sigma^*\pi^*)$  emission in pure acetonitrile; however, DMF solutions of **1** show terpyridine-localized  $^3(\pi\pi^*)$  emission. Terpyridine vibrations in the 1300 to 1700  $\text{cm}^{-1}$  range are enhanced in the resonance Raman spectra of complexes **1** - **4**, thereby confirming the  $\pi^*(\text{tpy})$  participation in the low energy transition.

Square planar  $d^8$  complexes show a pronounced tendency to aggregate as weakly metal-metal-bonded oligomers.<sup>1</sup> The most thoroughly investigated materials include infinite-chain  $\text{Pt}(\text{CN})_4^{2-}$  species<sup>2</sup> and several luminescent binuclear complexes (e.g.,  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$  and  $[\text{LL}'\text{Ir}(\mu\text{-pz})]_2$  ( $\text{LL}' = (\text{CO})_2$ ;  $(\text{CO})(\text{PR}_3)$ ; 1,5-cyclooctadiene);  $\text{pzH} = \text{pyrazole}$ ) that possess metal-metal-bonded  $d\sigma^*(d_{z^2})p\sigma(p_z)$  excited states.<sup>3</sup> Mononuclear  $\alpha$ -diimine complexes of  $\text{Pt}(\text{II})$  (e.g.,  $\text{Pt}(\text{bpy})(\text{CN})_2$  ( $\text{bpy} = \text{bipyridine}$ )) tend to crystallize as linear chains, and the highly luminescent solid materials are more intensely colored than the monomers.<sup>4</sup> These complexes exhibit luminescence spectra that occur at lower energy and have much different emission profiles than those for the  $\text{Pt}(\text{CN})_4^{2-}$  chains. It has been suggested<sup>4</sup> that the solid-state emission of this type of complex is attributable to a  $(d\sigma^* \rightarrow \pi^*(\alpha\text{-diimine}))$  excited state.

We have begun an investigation of the photophysics of  $d\sigma^*\pi^*$  excited states in discrete binuclear  $d^8$ - $d^8$  complexes containing polypyridyl ligands. Kostic has characterized  $\{[\text{Pt}(\text{tpy})]_2(\mu\text{-can})\}(\text{PF}_6)_3$  ( $\text{tpy} = \text{terpyridine}$ ;  $\text{can} = \text{canaverine}$ ),<sup>5</sup> and we have prepared related complexes with a variety of anionic N—N bridging ligands (Table I).<sup>6</sup> The colors of the compounds range from light orange (1) to deep red (3, 4). In addition to UV absorptions attributable predominantly to  $\pi\pi^*$  transitions, there are new visible absorption bands that, along with emission maxima, move to lower energy with decreasing Pt—Pt separation (Figure 1).<sup>7</sup> The solid-state luminescence spectra at ambient temperature for all these complexes exhibit featureless bands (Figure 1) that blue shift slightly at 77K (Table I); the excited-state lifetimes fall between 1 and 2.5  $\mu\text{s}$ . The 77K glassy solutions of 2, 3, 4 show similar luminescence profiles. Terpyridine vibrations ( $1300$  to  $1700\text{ cm}^{-1}$ ) are enhanced in the resonance Raman spectra of 1 - 4, thereby confirming that a tpy orbital is involved in the low-energy electronic transition.<sup>8</sup>

The emission spectra of the pyrazolyl-bridged complex (1) in a frozen acetonitrile solution and in the solid state are similar in appearance ( $\lambda_{\text{max}} 592\text{ nm}$ ); however, in frozen DMF ( $\text{DMF} = \text{dimethylformamide}$ ) solution or a 10:10:1 EtOH:MeOH:DMF glass, the emission blue shifts and is highly structured (Figure 2). Since similarly structured

emission bands are observed for  $\text{Pt}(\text{tpy})(\text{NH}_3)^{2+}$ ,<sup>9</sup>  $\text{Zn}(\text{tpy})\text{Cl}_2$ ,<sup>10</sup>  $\text{Ir}(\text{tpy})_2^{3+}$ ,<sup>11</sup>  $[\text{Pt}(\text{bpy})\text{en}](\text{ClO}_4)_2$  ( $\text{bpy}$  = bipyridine;  $\text{en}$  = ethylenediamine),<sup>4</sup> and terpyridine<sup>8</sup> itself, this feature is attributed to a tpy-localized  $^3(\pi\pi^*)$  transition. The striking result is that very small changes in solvent composition can cause the observed emission to change from the broad, poorly structured  $^3(d\sigma^*\pi^*)$  to the highly structured  $^3(\pi\pi^*)$  system. Apparently, the energy of the  $^3(d\sigma^*\pi^*)$  state depends strongly on the nature of the solvent, as expected for a state with MLCT character.

The fluid solutions of these new complexes in EtOH/MeOH/DMF do not show any significant emission intensity at room temperature, and there is essentially complete quenching of otherwise highly emissive glassy solutions when they are warmed through their glass transition temperature. This constitutes yet another distinction from the  $d\sigma^*p\sigma$  excited states of compounds such as  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4^{4-}$ , which are relatively long-lived in fluid solution.<sup>3a</sup>

It is apparent that the orbital configuration of the lowest energy electronic excited state in complexes 1 - 4 depends on the metal-metal separation. For shorter Pt-Pt distances, the lowest state is  $^3(d\sigma^*\pi^*)$ ; as the distance between the platinum atoms increases, the  $^3(d\sigma^*\pi^*)$  energy increases. At sufficiently large Pt-Pt separations, the  $^3(d\sigma^*\pi^*)$  state will move above  $^3(\pi\pi^*)$ . Interestingly, the  $\mu$ -pyrazolyl complex 1, which displays both  $d\sigma^*\pi^*$  and  $\pi\pi^*$  emission spectra, is very near this crossover.

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6. A related compound  $\{[\text{Pt}(\text{tpy})]_2(\mu\text{-guanidine})\}(\text{ClO}_4)_3$  has been reported: Kip, H.-K.; Che, C.-M.; Zhou, Z.-Y.; Mak, T.C.W. *J. Chem. Soc., Chem. Commun.* **1992**, 1369-1371. The relationship between the Pt-Pt separation (3.090(1), 3.071(1)Å) and the absorption spectrum ( $\lambda_{\text{max}}$  483 nm) of **5** accords with our findings. Kip, Che, and coworkers have observed weak emission ( $\phi = 1.27 \times 10^{-4}$ ) for **5** in fluid  $\text{CH}_3\text{CN}$  solution. We also have found very weak emissions from **1-4** in  $\text{CH}_3\text{CN}$  solutions.
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8. Unfortunately, attempts to determine  $\nu(\text{Pt}_2)$  (expected to be well below  $100 \text{ cm}^{-1}$ ) have thus far been unsuccessful.
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**TABLE I.** Structural and spectroscopic data for  $[\text{Pt}(\text{tpy})]_2(\mu\text{-L})^{3+}$  complexes.

<sup>a</sup> DMF solutions ( $\text{CH}_3\text{CN}$  solution for **3**) at room temperature. Molar absorptivity in parentheses. <sup>b</sup> Lowest energy feature. <sup>c</sup> Monitor lowest energy emission. <sup>d</sup> DMSO solution at room temperature; 442 nm He/Cd laser. <sup>e</sup> Reference 6a. <sup>f</sup> Solid at room temperature. <sup>g</sup> Solid at 77 K. <sup>h</sup>  $\text{CH}_3\text{CN}$  solution at 77 K. <sup>j</sup> 10:10:1 MeOH:EtOH:DMF glass at 77 K. <sup>k</sup> Reference 6b. <sup>l</sup> Reference 5.

**FIGURE 1.** Electronic spectra of **3**: — absorption at room temperature ( $\text{CH}_3\text{CN}$  solution); - - emission at 77 K (10:10:1 MeOH:EtOH:DMF); ----- excitation at 77 K (10:10:1 MeOH:EtOH:DMF).

**FIGURE 2.** Emission spectra of **1** at 77 K: —  $\text{CH}_3\text{CN}$  solution; - -  $\text{CH}_3\text{CN}/1\%\text{DMF}$ ; -----  $\text{CH}_3\text{CN}/1\%\text{MeOH}$ .

N—N	d(Pt—Pt) (Å)	Absorption $\lambda_{\text{max}}(\text{nm})^{\text{a,b}}$	Emission $\lambda_{\text{max}}(\text{nm})$	Lifetime $\tau(\mu\text{s})$	Excitation $\lambda_{\text{max}}(\text{nm})^{\text{b,c}}$	Raman $\Delta\nu(\text{cm}^{-1})^{\text{d}}$
$\mu$ -pyrazole ( $\mu$ -pz) 1	3.432(3) <sup>e</sup>	430(2520)	630 <sup>f</sup> 630 <sup>g</sup> 592 <sup>h</sup> 472 <sup>j</sup> 513 <sup>j</sup> 542 <sup>j</sup> 585 <sup>j</sup>	1.1 <sup>h</sup>	410 <sup>j</sup>	1338 1480
$\mu$ -azaindole ( $\mu$ -az) 2	3.113(2) <sup>k</sup>	460(2050)	690 <sup>f</sup> 678 <sup>g</sup> 639 <sup>j</sup>	2.50 <sup>j</sup>	497 <sup>j</sup>	1338 1481 1570 1606
$\mu$ -diphenylform- amidine ( $\mu$ -dpf) 3	3.049(3) <sup>k</sup>	490(3390)	712 <sup>f</sup> 710 <sup>g</sup> 670 <sup>j</sup>	2.51 <sup>j</sup>	515 <sup>j</sup>	1338 1482 1572 1606
$\mu$ -arginine ( $\mu$ -can) 4	2.998(2) <sup>l</sup>	488(3700)	730 <sup>f</sup> 715 <sup>g</sup> 690 <sup>j</sup>	<0.02 <sup>f</sup> 1.4(10 K) <sup>g</sup> 2.34 <sup>j</sup>	520 <sup>j</sup>	1338 1486 1572 1606

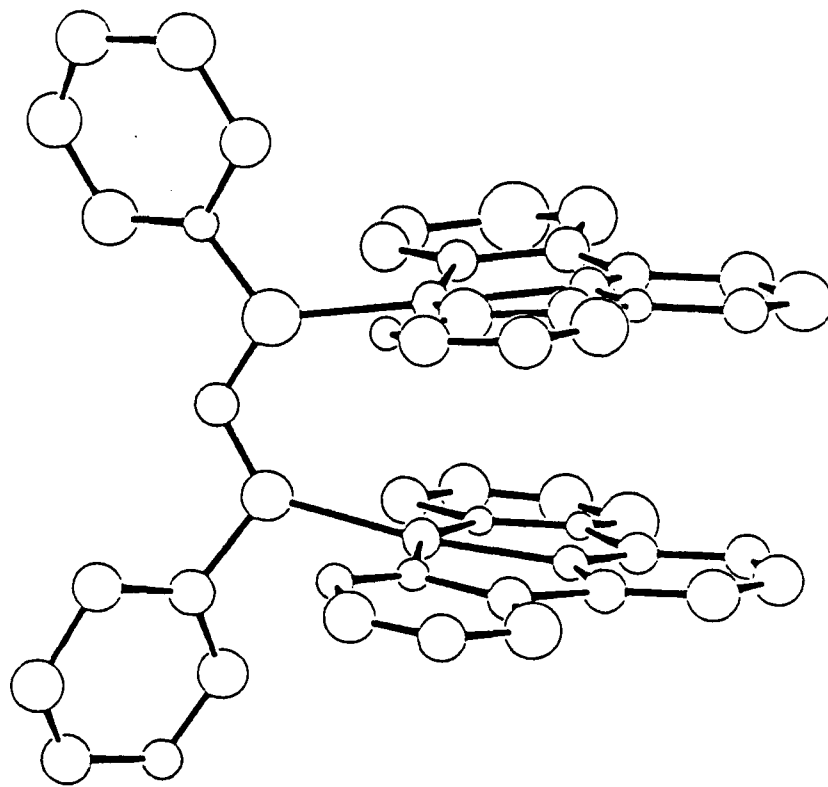


FIGURE 3.1

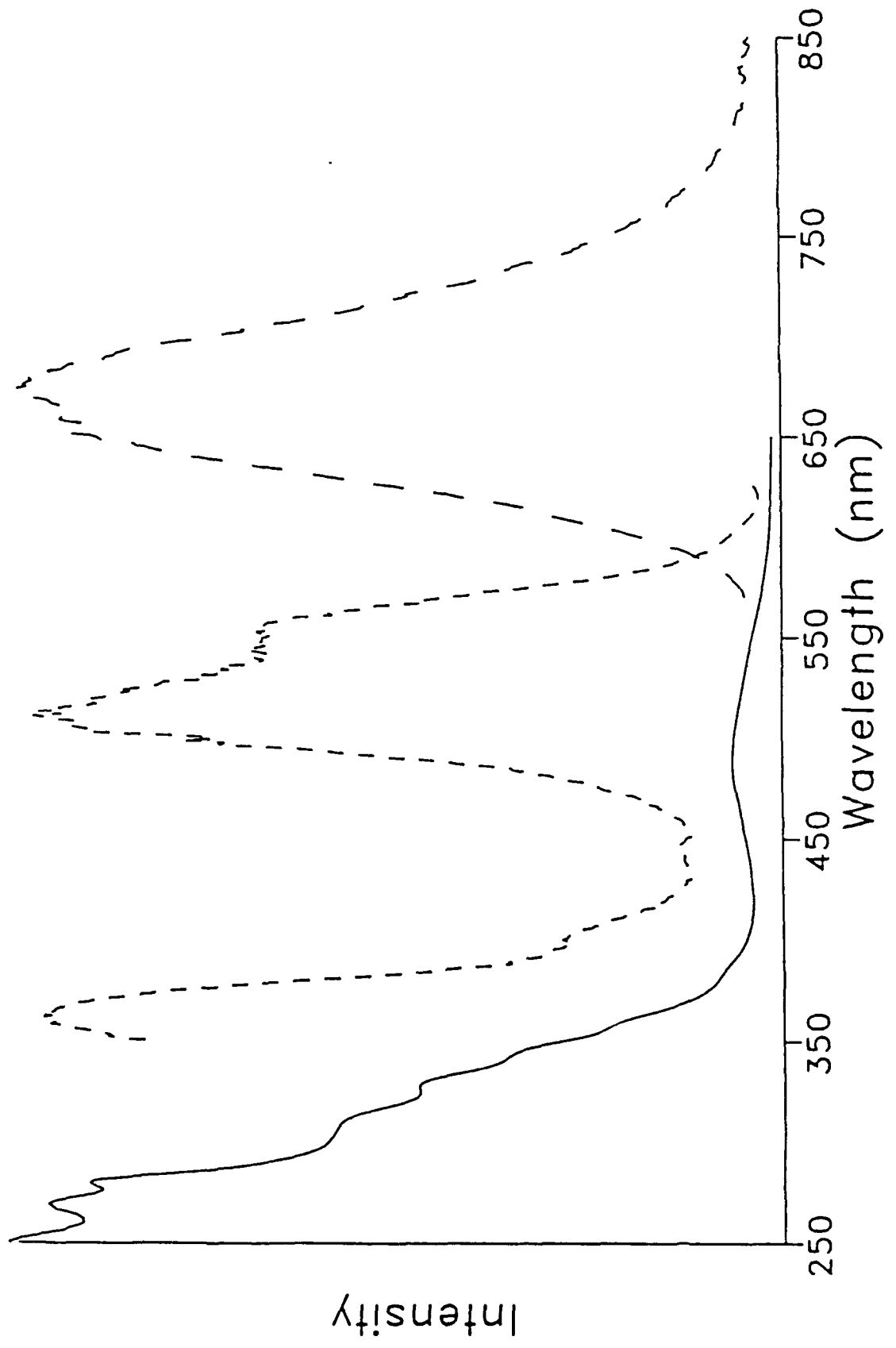


FIGURE 2

